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Electronic Spectra of 2, 6-dichlorotoluene

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The spectrum of 2, 6-dichlorotoluene in the vapour phase is found to consist of an allowed part with the 0-0 band at 36130 cm^{-1} and a forbidden part. It is discussed that the forbidden part appears due to mixing of the electronic state $^1B_2$, under consideration, with an upper state $^1A_1$ (derived from the $^1E_{1u}$ state of benzene) through the excitation of a b_2 vibration of excited state frequency about 460 cm^{-1}. The electronic spectra of 2, 6-dichlorotoluene are also examined in different phases and in solution. The observed small intensity of the bands ($\varepsilon_{max} \sim 78$-188) and the small f-value ($f=2.4\times10^{-3}$) indicate that the transition is weak. The assignments of the electronic bands in the vapour phase made by previous authors are revised.

1. INTRODUCTION

In discussing the electronic spectra of polysubstituted benzene molecules it was pointed out by Sklar (1942) that the migration moments due to various substituents in the phenyl ring may give a zero or nearly zero resultant whereby the spectra of such molecules arising from transition allowed by symmetry of the molescules, will be weak and will exhibit the features of a forbidden or a nearly forbidden transition. In such cases, borrowing of intensity from a strongly allowed transition nearby through excitation of vibrations of proper symmetry plays an important role (Craig and Gordon 1965, Herzberg 1966, Mallick and Banerjee 1974). As an example of such transition, the spectra of 2-6 dichloro-toluene molecule have been investigated. Mehrotra (1968) and Varodarajan and Kalkar (1975) had previously analysed the spectra of 2, 6-dichlorotoluene on the basis of an allowed transition with a strong 0-0 band. But actually the migration moment of the molecule should be small and the spectrum should be weak so that a re-examination of the spectrum seemed worthwhile. Therefore, spectra of the molecule in vapour phase, in the solid phase (90°K) and in a rigid glass in isobutyl alcohol (90°K) have been recorded and the features are discussed in this paper.

2. Experimental

The sample of 2-6 dichloro toluene were supplied by B.D.H. (England) and was used after fractional distillation. The solvent isobytyl alcohol, was also supplied by B.D.H. (England) and it was ascertained that the solvent had no absorption in the region studied. The absorption spectra were photographed on Kodak spectrum analysis No. 1 film with Adam Hilger El all metal quartz spectrograph (E 478) having a dispersion of 2.5 Å/mm in the region of 2600 Å. Microphotometric records were taken with a Kipp and Zonen moll microphotometer. The spectra were calibrated with iron arc spectra. The solution spectra were measured with a Beckman DU 2 spectrophotometer.

3. Results and Discussions

Taking the symmetry of 2, 6-dichloro toluene molecule as C_{2v}, the forbidden electronic transition $^1B_{2u} \leftarrow ^1A_{1g}$ of benzene becomes a symmetry allowed $^1B_2 \leftarrow ^1A_1$ transition. From the computed spectroscapic moments of the CH_3 group and the chlorine atom (Platt 1951), the resultant migration moment of 2, 6-dichloro toluene is only + 1. Actually the small intensities of the bands (ε_{max} ~ 70-188) and measured f-value of 2.4×10^{-5} of the transition (Table 1) substantiate the conclusion that the transition is weak.

Table 1. Spectrum of solution of 2, 6-dichloro toluene in isobutyl alcohol at room temperature (300°K)

Wave number in cm^{-1} (ν_{max})	ε_{max}	f-value
35800	70	
36300	136	
36917	—	
37067	—	2.42×10^{-5}
37358	188	
37850	143	
38465	144	

As can be seen from fig 2, the vapour phase spectrum exhibits weak and somewhat broad bands and in appearance resembles the spectra reported by the earlier authors (Mehrotra 1968, Varadarajan and Kalkar 1975). In the vapour spectrum the strongest band on the long wave length side is at

36446 cm^{-1} and it is accompanied by a weak hump on its red side at about 36130 cm^{-1}. Ordinarily, one would be inclined to assign the band at 36446 cm^{-1} as the 0, 0 band. Actually, Mehrotra (1968) assigned the

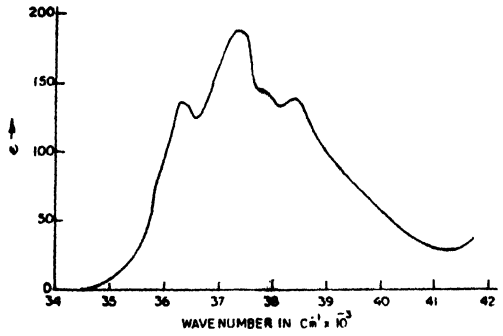
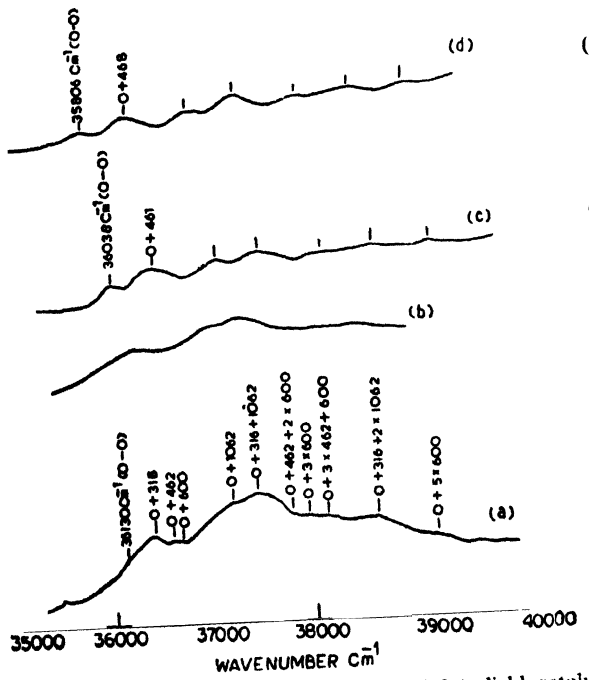


Fig. 1. Solution spectra of 2-6 dichlorotoluene in isobutyl alcohol at room temperature.



(d) Thin film at 90°K

(c) Rigid glass in isobutyl alcohol at 90°K.

(b) Isobutyl alcohol solution spectra at room temperature.

(a) Vapour.

Fig. 2. Near ultraviolet absorption spectra of 2-6 dichlorotoluene in different phase.

0-0 band to a strong band which he reported at 36506 cm^{-1}. Later, Varadarajan and Kalkar took a strong band at 36854 cm^{-1} as the 0, 0 band But in view of the small resultant moment (+1) of the 2-6 dichlorotoluene

molecule as stated earlier, the transition, though allowed, should be weak. Thus a reconsideration of the assignment of the 0-0 band and other features of the spectra is called for and in this regard, examination of the spectrum due to rigid glass in isobutyl alcohol at 90°K should be helpful. In the latter spectrum a band of moderate intensity persists at 36038 cm^{-1}, on the long-wave length side of the strong band at 36499 cm^{-1} (Fig. 2(c)). It is most unlikely that the 36038 cm^{-1} band arises from a $0 \leftarrow v$ transition at 90°K and this should more reasonably be taken as the 0-0 band of the absorption spectrum. A comparison between the vapour and rigid glass spectra indicates that the 36130 cm^{-1} band due to the vapour (corresponding to 36038 cm^{-1} band in rigid glass) does not represent a $0 \leftarrow v$ transition and should be attributed to the 0-0 transition instead of the strong band at 36446 cm^{-1} as was done by previous workers. The small intensity of the band is consistent with a weak transition due to small migration moment of the molecule.

As a first approximation, the molecule may be treated as having a C_{2v} symmetry. Of the active fundamental vibrations, besides those belonging to a_1 class, one b_2 vibration of frequency about 460 cm^{-1} is quite prominent (tables 2 and 3). The frequency 1062 cm^{-1} assigned to a_1 mode ν_6 in the excited state (table 3) can be alternatively expressed as a combination frequency 1062=462+600. Actually the band at 37192 cm^{-1} is broad and seems to consist of two unresolved close components so that a fundamental frequency 1062 cm^{-1} as well as a combination frequency of accidentally the same magnitude are probably involved.

Table 2. Absorption bands of 2, 6-dichlorotoluene in the vapour phase

Wave number in cm^{-1}	Assignment
36130 (w)	0 — 0
36446 (s)	0 + 316
36592 (s)	0 + 462
36730 (s)	0 + 600
37192 (vs b)	0 + 1062 ;
	0 + 462 + 600.
37498 (vs)	0 + 3 × 462 ;
	0 + 316 + 1062.
37767 (vs)	0 + 462 + 2 × 600.
37925 (s b)	0 + 3 × 600 ;
	0 + 316 + 462 + 1062.
38113 (s b)	0 + 3 × 462 + 600 ;
	0 + 316 + 600 + 1062.
38580 (s)	0 + 316 + 2 × 1062.
39130 (s)	0 + 5 × 600 ;
	0 + 316 + 600 + 2 × 1062.

Table 3. The 0-0 bands and active excited state vibrational frequencies in cm^{-1}

	Vapour	Isobuty alcohol rigid glass at 90°K	Solid (thin film) at 90°K	Assignment* and symmetry species
(0-0) band	36130	36038	35806	—
	316	(312)	(334)	ν_{10} (a_1)
	462	468	462	ν_{28} (b_2)
	600	(610)	(602)	ν_8 (a_1)
	1062	1070	1071	ν_6 (a_1)

*Green et al. (1971)

Cases of intensity borrowing through vibronic mixing of electronic states involving non-totally symmetric vibration in the forbidden transition in benzene (Herzberg 1966) and totally symmetric vibrations in the spectra of phenanthrene (Craig & Gordon, 1965) and 1, 2, 3,-trimethyl benzene (Mallick and Banerjee, 1974) are known. The b_2 vibration 460 cm^{-1} appears in the spectra both as a fundamental as well as in combination, excited several quanta. Explanation of the occurrence of non-totally symmetric b_2 vibration and the observed relative intensity of the bands involving odd quanta excitation of this vibration in the spectra of 2, 6-dichloro toluene may be offered in terms of vibronic mixing of the $^1B_2$ state of the $^1B_2 \leftarrow {}^1A_1$ transition under consideration with an upper $^1A_1$ state derived from the $^1E_{1u}$ electronic state of benzene through excitation of b_2 vibration. The $^1B_2 \leftarrow {}^1A_1$ transition may then borrow intensity from the allowed $^1A_1 \leftarrow {}^1A_1$ transition (Herzberg 1966). The general features of the spectra are reasonably explained by the analysis presented above.

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